A SOFTWARE FOR MODELING OPTICAL AND THERMAL RADIATIVE PROPERTIES [1]

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ABSTRACT

An analysis of the emittance of the MgO crystal is use to show both the necessity to have recourse to models of semi quantic dielectric functions for reproducing correctly thermal radiative properties and to present new tools for the spectroscopic community. A new XML-based format is proposed to encode modeling problems and mathematical representations of optical functions in a way that is both human readable and understandable by software applications. A curve fitting software based on this format is also presented. This tool has been used to obtain the results reported in this paper, it is freely available and it is able to construct very different types of dielectric models including classic and semi quantic ones.

KEY WORDS: curve fitting; dielectric function; emittance; magnesium oxide; osml.

1. INTRODUCTION

What is the current practice for analyzing optical spectra in material science? If one tries to answer this question by reviewing a representative set of publications, the following statement comes into view. Modeling is widely used and it is actually preferred to the classical inversion methods using the well-known Kramers-Kronig relations [1] or other phase retrieval procedures [2,3]. The main reason of such a preference comes certainly from the extra information provided by this method on the microscopic mechanisms responsible for the absorption, knowledge that is very useful for material researchers.
But even if this approach has known an undeniable success in the reproduction of very different kinds of reflectivity spectra and has given very important results concerning phase transitions [4-6], it remains that its use still presents some drawbacks. The classic dielectric function models currently used to simulate reflectivity data are not suitable for the analysis of transmittance and emittance spectra because of physical limitations; new expressions must be considered. Another serious problem is the lack of public software applications that are able to deal with the complexity and the variability of the optical function models, in a way that corresponds to the needs of the spectroscopic

community. As a consequence, reuse and comparison of the optical functions published by different groups are actually extremely difficult. This situation pleads in favor of the adoption by the spectroscopic community of a standard format for encoding spectroscopic models that is both human readable and understandable by software applications in order to facilitate data exchange.
This paper brings some elements to progress toward the resolution of the above problems. After introducing the semi quantic dielectric function models that do not have the limitations of the classic ones, a language able to store the complex mathematical representations of optical functions and a software application are presented. Finally, an example of treatment is shown.

2. CLASSIC MODELS LIMITATIONS – SEMI QUANTIC MODELS

The quality of the results obtained with a modeling method depends largely on the ability of its mathematical expressions to recreate in detail the spectral dependence of the intrinsic properties of a material. For example, classic dielectric function models such as the sum model:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j \Omega_{jTO}^2}{\Omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega},$$

or the generalized factor model:

$$\frac{\varepsilon(\omega)}{\varepsilon_\infty} = \prod_j \left(\frac{\Omega_{jLO}^2 - \omega^2 + i\gamma_{jLO}\omega}{\Omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega} \right) - \frac{\Omega_p^2 + i(\gamma_p - \gamma_0)\omega}{\omega^2 - i\gamma_0\omega},$$

where Ω_{TO}, Ω_{LO}, Ω_p represent respectively the transverse optic, longitudinal optic and plasma frequencies, γ_{TO}, γ_{LO}, γ_p, γ_0 are the associated dampings and $\Delta\varepsilon$ is the dielectric strength of the oscillator, have been successfully used to simulate the infrared reflectivity spectra of very different kinds of materials but are clearly inadequate to analyze their transmittance and emittance spectra. As a matter of fact, these expressions describe correctly the optical response of materials in their opaque spectral regions but largely overestimate the absorption coefficient in the transparent and semi-transparent regions where the multiphonon and impurity absorptions stand. This is why classic models are good enough to reproduce reflectivity spectra but are definitely not good ones to simulate other quantities. To correctly reproduce the optical response between the far infrared to the near ultraviolet range, new forms of dielectric function models must be introduced. Semi-quantic models [7,8] where phonon terms include self-energy functions do not have such limitations and are particularly useful for modeling emittance spectra, as we will see later. The semi quantic version of the sum model is the following:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j \Omega_j^2}{\Omega_j^2 - \omega^2 + i\gamma_j(\omega)}.$$

In this expression, the self-energy functions $\gamma_j(\omega)$ that can have a rather complex spectral dependences substitute the damping terms of the classic version.

3. OPTICAL SPECTROSCOPY MARKUP LANGUAGE

Exchanging data in a standard way is a rather general preoccupation. Indeed, standard formats for experimental data exchange between instruments and software applications already exist. One can cite the largely diffused format JCAMP-DX (named after the Joint Committee on Atomic and Molecular Physical Data - Data eXchange) which is a set of industry-wide standard protocols for transfer of spectroscopic data sets, sponsored by the International Union of Pure and Applied Chemistry (IUPAC) [9]. Another example is the Generalized Analytical Markup Language (GAML) that is an XML-based file format for storing analytical instrument data [10]. These two formats represent a valuable effort in the direction of the standardization of experimental data exchange and is an encouragement to do the same for diffusing spectroscopic models and mathematical representations of optical properties.

Actually there are two main markup languages specialized in the reproduction of mathematical expressions: *OpenMath* [11] and *MathML* [12]. These two languages are in principle able to respond to our needs in terms of mathematical construction, but in practice they are too general and it is more convenient to construct a new one that reflects more the specific needs of the spectroscopic community. The advantage of a new language is the possibility of beneficing of the existing experience in mathematical construction and to add new elements to take into account of the particularities of the domain. For example, a document protection scheme is necessary to secure the content of spectroscopic model documents and files containing mathematical representations of the optical properties of materials.

The Optical Spectroscopy Markup Language (OSML) has been written to fit these needs. OSML is an XML-based format and thus profits of the power of XML for representing structured documents in a standardized and application independent way. The design of the format was made as simple as possible to facilitate its widespread. Its structure is sufficiently flexible to easily reproduce no solely all real or complex expressions that can be expressed with the elementary functions but also the set of interconnected mathematical expressions that represents the essence of a modeling problem (physical definitions of experimental quantities, models for the intrinsic properties and other derived expressions). An extension mechanism is also present, besides the core function library provided with the language that regroups elementary and general use spectroscopic functions; users can create new libraries to store functions of a specific domain. A full description of this format is given at the following web site [13].

4. MODELING SOFTWARE

FOCUS is a software application freely available on the web [14] that has been developed to facilitate the production and the diffusion of OSML documents. This software application owns a very versatile mathematical core that is able to construct, in a visual way, any set of interconnected mathematical expressions that can be written with the optical spectroscopy markup language. The application does not make any assumption on the form of the mathematical expressions and thus is able to reproduce easily classic and semi quantic models whatever their complexity, to take into account for multiple reflection effects, interference effects, incident angle dependence, effective medium theories and much more. Its interface allows to create OSML libraries and to

use external functions as built-in ones. The software is also a powerful curve fitting program that implements both graphical and automatic adjustment modes and other tools to ensure a rapid analysis of all kinds of experimental spectra. Results of simulation can be exported in various file formats. The results presented in the following have been obtained with this program.

5. EMITTANCE OF THE MAGNESIUM OXYDE

As shown by the Kirchhoff relations, emissivity measurements combine both the information contained in reflectance and transmittance spectra. Such data are then sufficient to obtain all the optical functions of a material, i.e. dielectric function, refractive index, conductivity, absorptivity and other experimental quantities.

One presents here an analysis of the emittance spectra of a 1 mm thick crystal of magnesium oxide at room temperature. This material, which has a relatively simple spectrum, is a good candidate to show the limitations of the classic models and the necessity to have recourse to more sophisticated ones. For this crystal, group theory predicts a single infrared active phonon mode, while the experiment shows a rather complex structure that cannot be adjusted with a single classic phonon term.

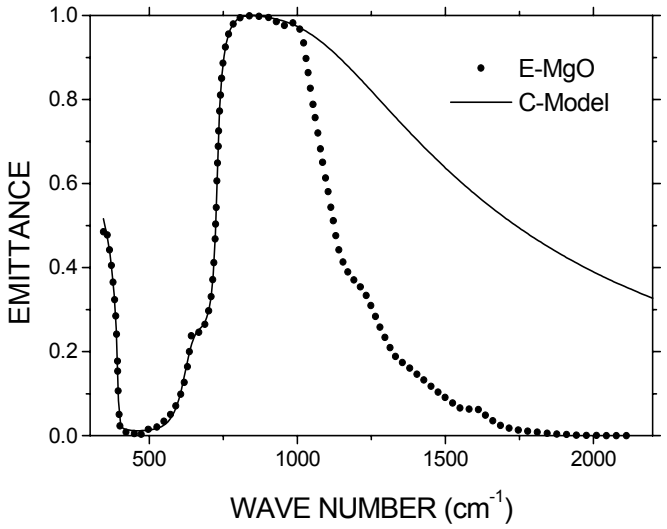

Fig. 1. Experimental emittance of a 1mm thick MgO crystal (circles) and best fit obtained with a classic dielectric function model (solid line).

As one can see in figure 1, the only way to reproduce the reflection band situated between 400 and 1000 cm^{-1} is to introduce two phonon terms. Even if the classic sum model gives a reasonable adjustment in this opaque region, it remains that this solution is not a physical one and it clearly unfits the spectral region above 1000 cm^{-1}.

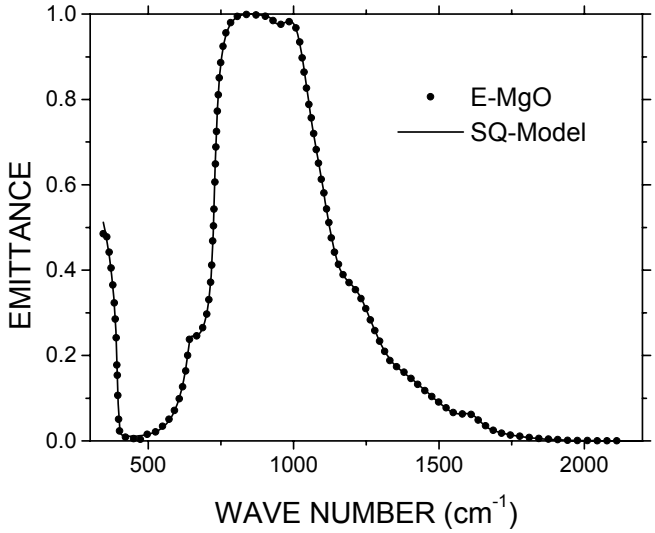

Fig. 2. Experimental emittance of MgO of a 1mm thick MgO crystal (circles) and best fit obtained with a semi quantic dielectric function model (solid line).

On the other hand, a semi quantic model containing a single phonon term is able to reproduce correctly the whole spectrum (figure 2). This new solution has a solid physical basis and gives no solely useful information on first order absorption but also on the multiphonon

processes that are responsible for the rather complex structure of the spectrum. The mathematical expression of the semi quantic dielectric function model used to reconstruct the experimental spectrum is the following:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_j \Omega^2}{\Omega^2 - \omega^2 + i\gamma(\omega)}.$$

where the self-energy of the anharmonic phonon is given by:

$$\gamma(\omega) = \sum_i G_i(\omega) + \sum_i L_i(\omega),$$

$G_i(\omega) = A_i e^{-4\ln(2)\left(\frac{\omega - x_i}{\sigma_i}\right)^2}$ is a gaussian function and

$$L_i(\omega) = \begin{cases} A_i e^{\left(\frac{\omega - x_i}{p_i^l}\right)} & \omega < x_i \\ A_i e^{-\left(\frac{\omega - x_i}{p_i^r}\right)} & \omega \geq x_i \end{cases}$$ is a generalized laplace function.

To correctly reproduce the spectral dependence of the self energy, it was necessary to introduce 3 generalized laplace functions and 5 gaussian functions. The generalized laplace functions have a shape that is adequate to describe anharmonic interactions involving two phonons, while gaussians are more suitable to reproduce the optical response of high order ($n \geq 3$) multiphonon processes. A representation of the self-energy function is reported in figure 3 and the values of the adjustable parameters of the dielectric function model are given in the table I.

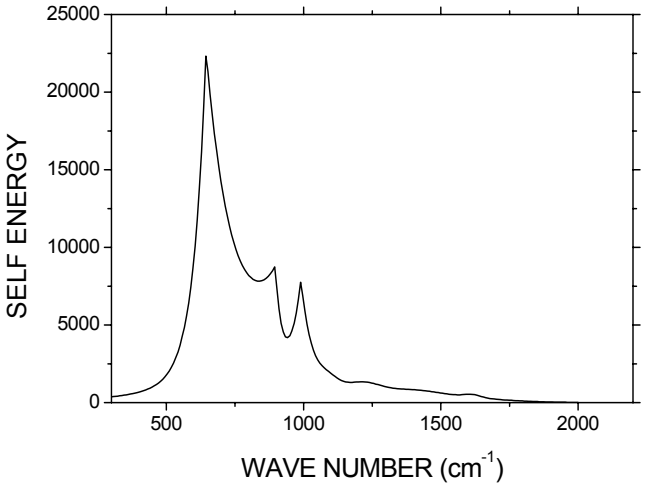

Fig. 3. Spectral dependence of the self-energy function characterizing MgO.

Global parameters	ε_∞	$\Delta\varepsilon$	Ω	
	2.95	6.98	396.39	
Self energy parameters	A_i	x_i	σ_i or p_i^l	p_i^r
L_1	20810	644.72	44.66	94.27
L_2	6568	896.90	206.11	23.17
L_3	7187	989.85	42.26	45.59
G_1	710.04	1089.07	94.29	
G_2	860.32	1209.43	158.68	
G_3	323.18	1380.4	227.86	
G_4	497.29	1426.32	496.89	
G_5	183.12	1613.74	70.59	

Table I. Parameter values of the semi quantic dielectric function model used for the reproduction of the MgO emittance.

All the above information was easily encoded in the following secure OSML document:

```
<?xml version=1.0?/>
<!-- Dielectric function model of MgO : 350 - 2500 cm-1 -->
<!-- Units : Wave Number (cm-1) -->
<osml version="1.0">
  <secure algorithm="SHA-256">
    29FC3E03 E3734320 E62092B0 57D1B849 356B3928 C8F1075F 5298DEFF
    2232A4F2
  </secure>
  <math>
    <definition name="x">
    </definition>
    <definition name="E-MgO">
      <apply>
        <function name="sum" source="core"/>
        <number> 2.95 </number>
        <apply>
          <function name="phonon-anharmonic-i" source="core"/>
          <link> x </link>
          <number> 6.98019 </number>
          <number> 396.392 </number>
          <apply>
            <function name="sum" source="core"/>
            <apply>
              <function name="laplace" source="core"/>
              <link> x </link>
              <number> 20809.6 </number>
              <number> 644.723 </number>
              <number> 94.267 </number>
              <number> 44.6646 </number>
            </apply>
            <apply>
              <function name="laplace" source="core"/>
              <link> x </link>
              <number> 6567.72 </number>
              <number> 896.901 </number>
              <number> 23.1655 </number>
              <number> 206.111 </number>
            </apply>
            <apply>
              <function name="laplace" source="core"/>
              <link> x </link>
              <number> 7186.99 </number>
              <number> 989.853 </number>
              <number> 45.5875 </number>
              <number> 42.2601 </number>
            </apply>
```

```
            <apply>
              <function name="gaussian" source="core"/>
              <link> x </link>
              <number> 710.038 </number>
              <number> 1089.07 </number>
              <number> 94.288 </number>
            </apply>
            <apply>
              <function name="gaussian" source="core"/>
              <link> x </link>
              <number> 860.322 </number>
              <number> 1209.43 </number>
              <number> 158.678 </number>
            </apply>
            <apply>
              <function name="gaussian" source="core"/>
              <link> x </link>
              <number> 323.179 </number>
              <number> 1380.4 </number>
              <number> 227.862 </number>
            </apply>
            <apply>
              <function name="gaussian" source="core"/>
              <link> x </link>
              <number> 497.289 </number>
              <number> 1426.32 </number>
              <number> 496.889 </number>
            </apply>
            <apply>
              <function name="gaussian" source="core"/>
              <link> x </link>
              <number> 183.116 </number>
              <number> 1613.74 </number>
              <number> 70.59 </number>
            </apply>
          </apply>
        </apply>
      </apply>
    </definition>
  </math>
</osml>
```

What are the advantages of such a representation? Firstly, the protection scheme and the fact that documents are directly generated by software applications warrant the integrity of the data encoded in a document. Secondly, the mathematical representations of physical properties or other physical models contained in these files can be reuse without any modification by software that implements OSML. This saves a lot of time,

avoids error typing and promotes data exchange. Finally, the format still is human readable with a little practice.

6. CONCLUSION

The creation of a new format (OSML) for exchanging spectroscopic models and mathematical representations of optical functions and the development of a public curve fitting software based on this format represent a first tentative to standardize data exchange and to propose a common tool to the spectroscopic community that is able to deal with the increasing complexity and variability of the models used for the reproduction of different kinds of optical spectra.

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14. Focus Home Page http://www.cnrs-crmht.fr/pot/software/focus.html